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Chemical corrosion of sanitary glazes of variable grain size composition in acid and basic aqueous solution media

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Abstract

Glazes are responsible for the majority of the final surface properties of ceramic products, including their chemical corrosion resistance in contact with solutions of either acid or alkaline reaction. It is known that by adjusting their molar compositions it is possible, to some extent, to control the reactivity of glazes with such solutions. However, the allowable range of molar composition changes is limited, because this would, at the same time, modify other glaze parameters, such as fusibility, colour, gloss, or hardness. The investigation results presented in the article demonstrate that there is a potential for a significant improvement in the chemical corrosion resistance and other surface parameters of glazes through selecting the grain size of particular groups of raw materials used. On the example of glazes intended for sanitary products it has been proved that the proper selection of the grain size of quartz, feldspars and all rest raw materials results in a distinct reduction of the degree of corrosion caused by the action of water solutions of NaOH and HCl.

Key words : Chemical resistance; Surface quality; Glossy; Glaze

1. Introduction

Ceramic glaze is a mixture of specified raw materials, which, after being ground and applied onto a ceramic body, is transformed, either wholly or partially, into a vitrified coat during a firing process. Glaze renders the surface chemically neutral, impermeable to liquids and gases, easy to clean, smooth, abrasion and scratch resistant and mechanically tough, and also enhances the aesthetic qualities of the product [1,2]. In the design of ceramic glazes, numerous factors must be taken into account, the most important of which include: the type of ceramic material onto which the glaze is to be applied, and the firing parameters. Any potential loads (*mechanical*, *chemical*, *thermal*, *etc.*) that the finished product is likely to encounter during its use need also to be considered [1,2].

One of the most important reasons for using glazes is their relatively high resistance to the corrosive action of various chemical agents. Literature describes general mechanisms of action of aqueous solutions of acids and bases on the glaze surface [3], though these are chiefly applicable to the study of the corrosion of glasses. New publications related to the corrosion of glazes have come out in recent years [5–8,10], but given the technological progress in ceramics and household chemistry, the information provided therein is not sufficient. It should be noted that the majority of glazes being currently in use are type composites of silicate and aluminosilicate polycrystals in a glass matrix. Even transparent glazes, resembling glass in appearance, do differ from glasses in composition, and primarily higher contents of aluminium oxide and bivalent alkaline earth metal oxides and lower contents of alkaline metal oxides [1].

Two mechanisms of chemical corrosion of glass are known. The first of them relates to the action of acids, and the other – of bases. Acids have a readily releasing hydrogen ion that can easily exchange alkali ions in the intermolecular network, changing them gradually into hydrated silicates. When the glass network is low in alkali the free silica - hydrate gel are formed on the surface. In a subsequent phase, this solution is washed out, and the silicic acid forms a more or less uniform thin film on the surface, which slows down the diffusion of ions and

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Table 1
Mole composition (mol%) of experimental glazes.

Oxide composition of experimental glaze (mol%)	
SiO_2	1.05
Al_2O_3	0.11
$Na_2O + K_2O$	0.23
CaO	0.13
MgO	0.03
ZnO	0.03
$ZrSiO_4$	0.06

inhibits the corrosion process. Removing this coat by any means exposes the next glass layers, and the process starts from the beginning [3,4].

In reaction with glass, bases can form soluble compounds with silicon. At the initial stage of corrosion, the process of OH^- ion absorption on oxygen in the Si–O–Si bridge is observed, which then results in breaking of these bonds. This is a dissolution process, whereby the components pass into the solution in the same proportions in which they occurred in the glass. The degree of corrosion depends on the surface properties and on the strength of the glass structure, as well as on the type and concentration of the alkali solution and on the temperature and time [3,4].

In water, the both mechanisms proceed simultaneously. Which of them plays the decisive role depends on the temperature and glass composition and structure. This type of corrosion is the least understood and described [3,5,9].

Until now, the improvement of the chemical resistance of glazes has been sought primarily in the changes of chemical composition [2–4,6,9]; in approximation, it is known how the change in selected oxides may influence the chemical corrosion [1–3]. The present paper reports results concerning the effect of the selective grinding of hard raw materials on the chemical resistance of ceramic glazes. It has already been proved [11] that the selection of the grain size of raw materials in the material batch helps to improve the surface properties of glazes, such as gloss, whiteness and smoothness. And since any surface defects are the locations of corrosion initiation, their elimination should lead to an increase in resistance to chemical corrosion.

2. Materials and methods

A dozen or so experimental glazes intended for sanitary products were prepared based on the uniform molar composition (Table 1). The glazes were prepared using the selective grinding technology developed and described in detail by the authors [11]. Hard raw materials, i.e. feldspars and quartz, were ground separately up to the specified grain size (Table 2) using an ‘‘agitator bead’’ type MicoCer laboratory mill supplied by Netzsch. The remaining components (talc, wollastonite, kaolin, ZnO) were prepared through joint grinding in a planetary mill to a residue of 0.2% on the 56 μm-mesh sieve. The final composition of the experimental glazes was created by homogenizing the above-mentioned raw material groups in the planetary mill for 15 min. So prepared glazes differed from each other in quartz grain size with a constant feldspar grain size, or in feldspar grain size with a constant quartz grain size.

Table 2
Grain size range of hard materials.

Medium grain size of raw materials range (μm)	
Faldspar	14.47–0.27
Quartz	8.83–0.47
Other	$5 < x < 56$

The prepared glazes were applied onto 6 cm diameter discs made from commercial sanitary body and fired in a chamber furnace at a temperature of 1230 °C for a total duration of 10 h. The specimens were subjected to corrosive action by three agents: water solutions of HCl (pH 1.8), NaOH (pH 13.5), and a commercial ceramic sanitary ware cleaner (pH 9.5), at a temperature of 40 °C for a duration of 48 h. The method of effecting the chemical corrosion is illustrated in Fig. 1. The basic parameter used for the evaluation of the degree of chemical corrosion of the glaze surfaces was the change in glaze surface gloss after corrosion, relative to the measurements made prior to corrosion, and expressed in percents. Gloss is a typically physical feature which relies on the light reflection law. To satisfy this law, a body must have, among other things, a smooth and flawless surface. Therefore, any surface defect caused by chemical corrosion should also cause a change in the gloss of that surface. Gloss measurements were performed using a X-Rite Elcometer 406L. A small measurement area (of a diameter of 3 mm) allowed the average gloss value of the entire corroded surface to be obtained. The surface gloss change results as a function of quartz and feldspar grain size are represented in Figs. 2 and 3.

Surface changes caused by corrosion were also determined by measuring the surface roughness before and after the corrosion. The measurements were carried out with a Hommel

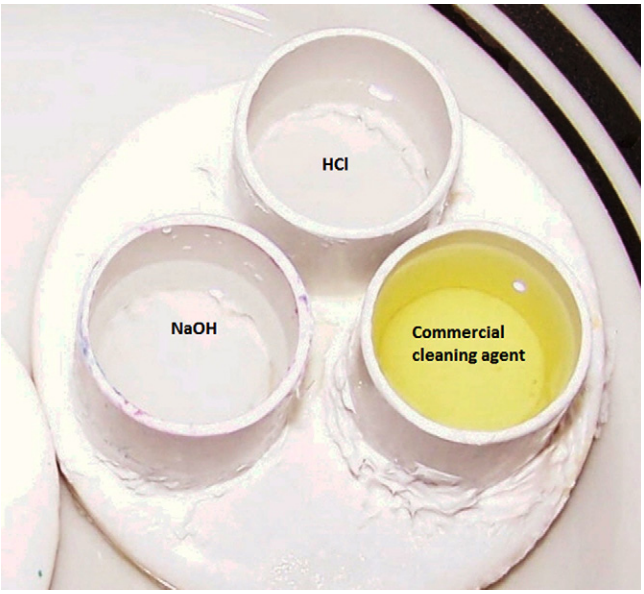

Fig. 1. The method of the tests of chemical corrosion on the samples of sanitary glazes.

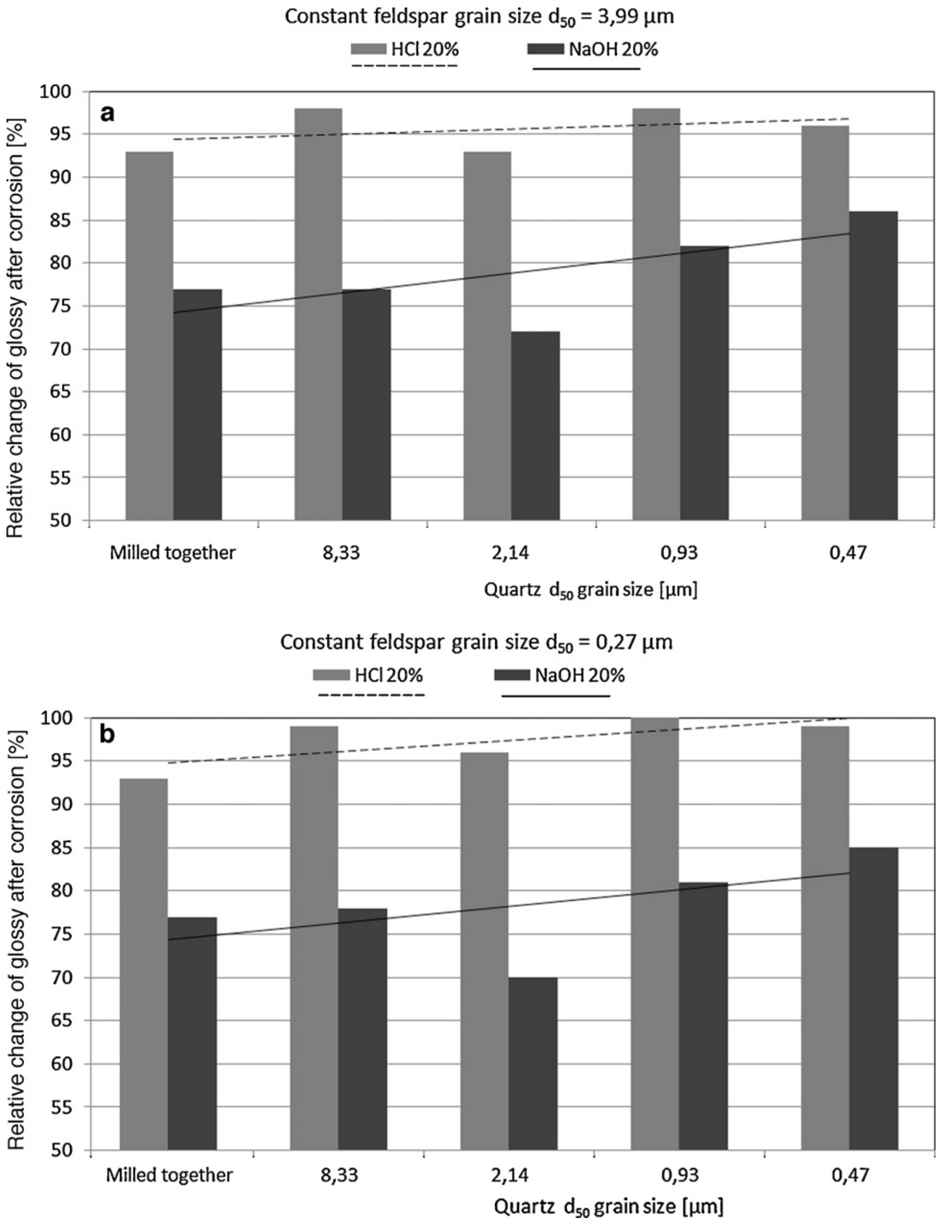

Fig. 2. Relative change of gloss of surface of samples of glaze after chemical corrosion in 20% water solutions HCl and NaOH in the function grain size of quartz and constant grain size of feldspar.

Tester profilometer. The results of these measurements are given in Table 3.

In addition, an attempt was also made to determine the corrosive effect of the three chemical agents tested on the glaze surface condition by observing the surfaces of uncorroded and corroded glazes using a Nikon AZ 100 optical microscope (Figs. 4–6).

Measurements of the mass loss from the surfaces of fired glaze pellets were also made after 240 h of chemical corrosion in acid and alkali solutions at a temperature of 40 °C (Figs. 7–11).

3. Results and discussion

The obtained results indicate a distinct relationship to exist between the grain size of quartz and feldspar and the degree of corrosion caused by the action of the three chemical substances used (i.e. 20% *aqueous solutions* of HCl and NaOH and the *commercial cleaner*).

The initial observations have shown that reducing the grain size of the hard raw materials down to a value below 500 nm has a favourable effect on the surface quality of the glazes examined (Figs. 4a and 5a). All of the observed photographs from the optical microscope show an increase in the smoothness of the surface with a smaller number of defects, as a function of decreasing quartz and feldspar grain size. This is confirmed by the decreasing values of the surface roughness, R_A, as a function of quartz grain size (Table 3).

The identical observations apply to the degree of chemical corrosion. The gradual reduction of quartz and feldspar grain size causes an increase in the chemical resistance of glazes

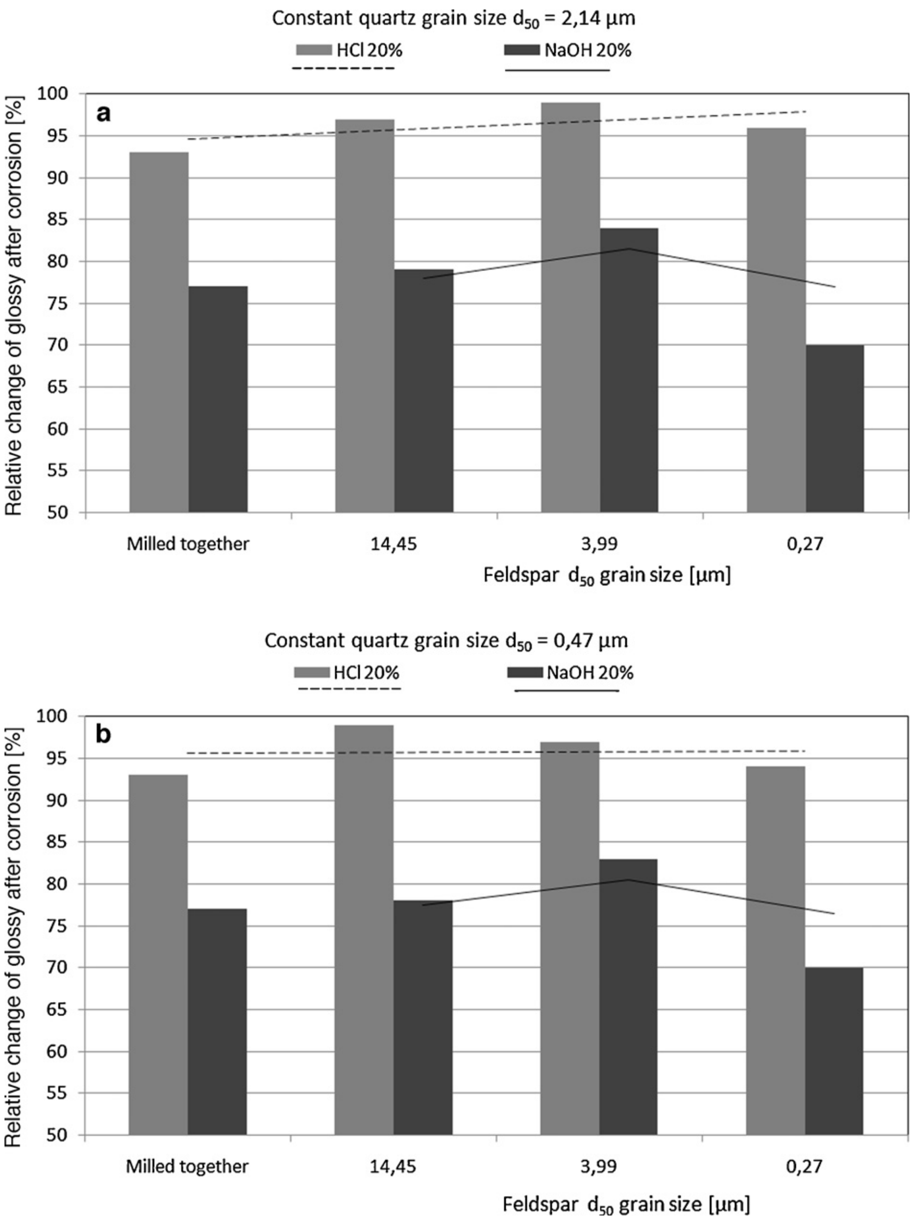

Fig. 3. Relative change of gloss of surface of samples of glaze after chemical corrosion in 20% water solutions HCl and NaOH in the function grain size of feldspar and constant grain size of quartz.

Table 3
Roughness of the surface of glazes before and after chemical corrosion.

Description	Commercial sanitary glaze	Experimental glaze				
	Glaze medium grain size (µm)	Quartz medium grain size (µm)				
	8.81 Roughness (µm)	8.33	0.47			
	R_A	Standard deviation	R_A	Standard deviation	R_A	Standard deviation
Before chemical corrosion	0.10	0.06	0.09	0.05	0.07	0.03
After commercial cleaning medium treatment	0.12	0.02	0.11	0.04	0.11	0.02
After HCl solution treatment	0.10	0.03	0.12	0.04	0.09	0.04
After NaOH solution treatment	0.12	0.03	0.12	0.03	0.10	0.03

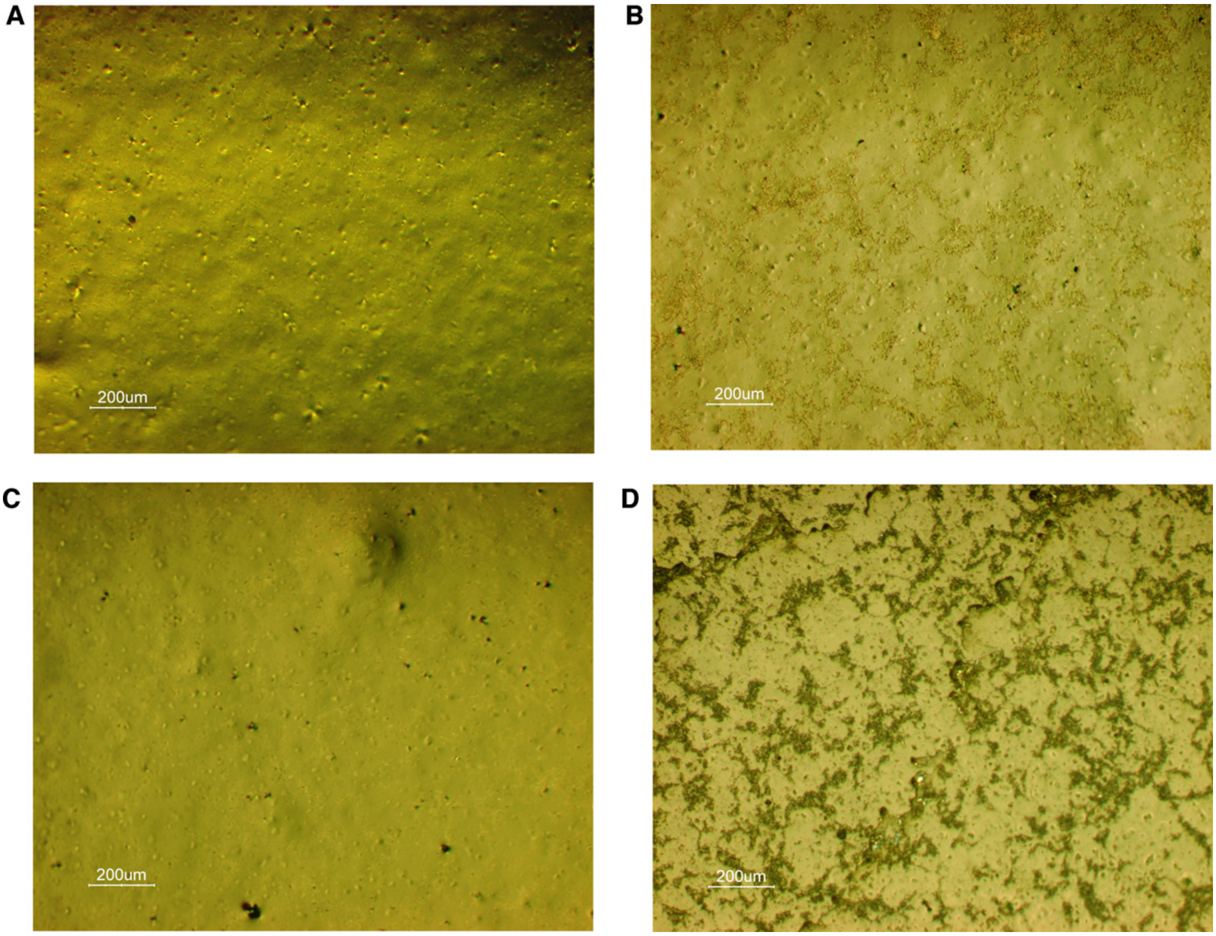

Fig. 4. Experimental glaze with coarsest quartz grains: (a) glaze surface without chemical treatment; (b) glaze surface after chemical treatment (commercial cleaning medium); (c) glaze surface after chemical treatment (20% water solution of HCl); (d) glaze surface after chemical treatment (20% water solution of NaOH).

(Figs. 2 and 3). In this combination, the change of the grain size of quartz comes out more advantageously (Fig. 2); here, the increase in chemical resistance with all the three corrosive agents is more distinct. Interesting is, however, the decrease of resistance for grain size values below approx. 1 μm, which requires to be further investigated. Reducing the grain size of feldspars also favourably influences the chemical resistance, but to a lesser extent than that of quartz (Fig. 3). These observations have their confirmation in the presented macroscopic photographs of corroded glaze surfaces (Figs. 4b–d and 5b–d). On the surfaces of glazes in which the finest grain size quartz has been used, a considerably smaller corrosion degree is observed (Fig. 5b–d). This is particularly well visible on the surfaces subjected to corrosion by the sodium hydroxide solution that is regarded as the strongest corrosive agent. In the case of applying the hydrochloric acid solution or the commercial cleaner, the corrosion degree is smaller for using the finer grains of both quartz and feldspar.

These observations are also confirmed by glaze surface roughness measurements. Firstly, the surface prior to the corrosion is characterized by higher smoothness, and the pits formed on the corroded surface are also smaller (Table 3). Although, in this case, the results need to be approached with greater cautiousness. In the case of acid corrosion, the soft silica gel formed can be easily removed by the diamond gauging point, which might slightly distort the results. In contrast, in the case of corrosion by alkali solutions, the dissolution of the siliceous-oxygen frame is non-uniform, being dependent on the force of bonds with the ions modifying the glaze structure. Thus, the increase in surface irregularities can be directly related to the corrosion degree.

Similar relationships were observed when measuring the mass loss of pellets made from fired glazes after 240 h of chemical corrosion in 20% solutions of hydrochloric acid and sodium hydroxide. The reference results in this case are the mass losses of the same glaze as prepared by the classical method of joint grinding of all components. The obtained results in each case show enhanced resistance to chemical corrosion. By reducing the grain size of quartz by ($d_{50} = 14.47$ μm), with a coarse feldspar grain size, very high chemical resistance to the action of hydrochloric acid was achieved, irrespective of the quartz grain size (Fig. 7). In

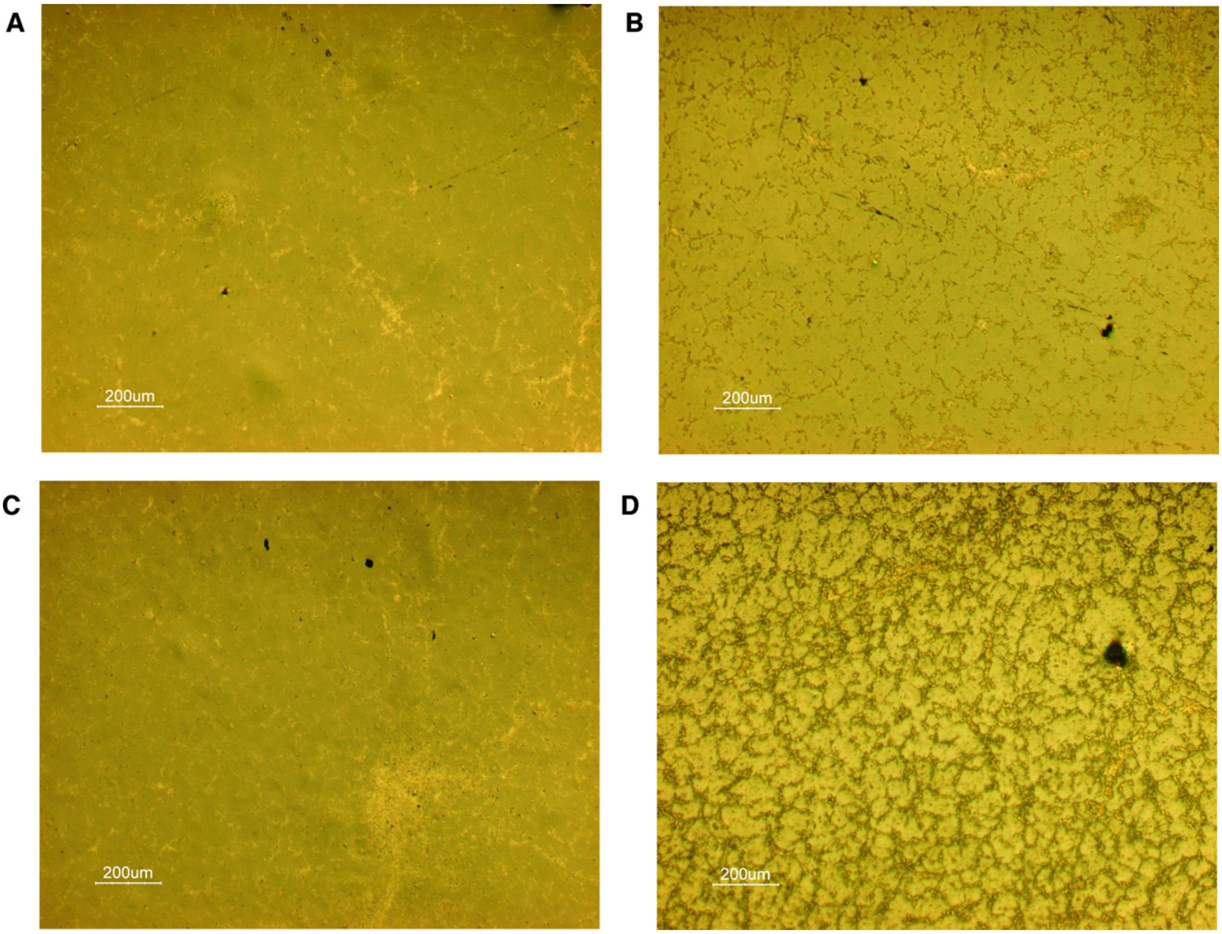

Fig. 5. Experimental glaze with finest quartz grains: (a) glaze surface without chemical treatment; (b) glaze surface after chemical treatment (commercial cleaning medium); (c) glaze surface after chemical treatment (20% water solution of HCl); (d) glaze surface after chemical treatment (20% water solution of NaOH).

the same case, the resistance to the action of sodium hydroxide attains a maximum for intermediate quartz grain sizes, and for a very fine grain size ($d_{50} = 0.47$ μm) it decreases again. When using very fine-grained feldspar ($d_{50} = 0.27$ μm) and reducing the quartz grain size (Fig. 8), a decline in chemical resistance to the action of NaOH is observed at the finest quartz grain size being equal to $d_{50} = 0.47$ μm. In the case of corrosion caused by HCl, the highest resistance is visible for coarse quartz grains ($d_{50} = 8.33$ μm) and a drop in resistance when finer quartz grains ($d_{50} = 0.93$ and 0.47 μm) are used. In the second series, corrosion was examined as a function of feldspar grain size at a constant quartz grain size (Figs. 9–11). In the case of quartz grains of a size of $d_{50} = 8.33$ μm, very high resistance to acid action was achieved, regardless the feldspar grain size. If we use quartz of an average grain size of $d_{50} = 0.93$ μm, we will still obtain good resistance to the action of hydrochloric acid and an increase in resistance to NaOH action with increasingly smaller feldspar grains. The use of the finest-grained quartz reduces the chemical resistance to both of the agents applied compared to the previous cases, though it remains higher than the resistance of the reference glaze.

All the above results appear to be true; a finer grain size of quartz promotes its faster melting and better melt homogenization, and thereby the formation of a more compact quartz structure providing a frame for the network of chemical bonds in the glaze. In contrast, finer grains of feldspars accelerate the process of melting of the whole glaze mass and reduce the melt viscosity. Under such conditions, the diffusion of modifying ions, especially the highly mobile alkaline and alkaline earth metal ions, is easier. The higher mobility of cations favours their volumetric homogenization and easier interaction with the molten quartz, whereby they form new bonds with the quartz and effectively build into the silica structure. However, feldspars, as the raw materials, are not responsible for the creation of the glaze network, but only support this process. Therefore their influence on the ultimate properties is less significant than that of quartz (Fig. 3), and using a lightly coarser grain size of this raw material is possible.

The lower glaze melt viscosity obtained through the finer grains of the hard raw materials certainly facilitates also the elimination of many surface defects, thanks to which the initiation of the destructive action of corrosive solutions is more difficult, as can be seen on the presented microscopic photographs.

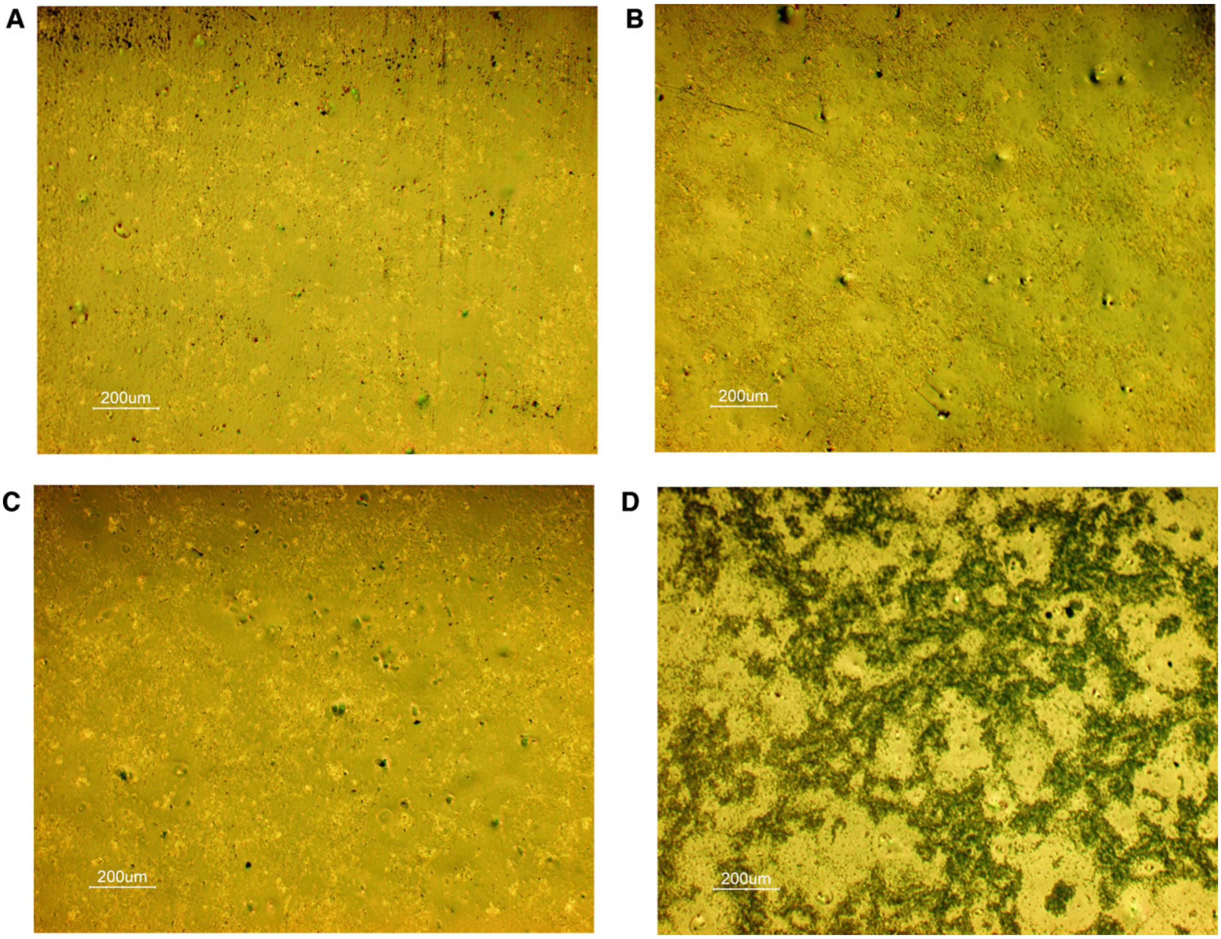

Fig. 6. Commercial sanitary glaze: (a) glaze surface without chemical treatment; (b) glaze surface after chemical treatment (commercial cleaning medium); (c) glaze surface after chemical treatment (20% water solution of HCl); (d) glaze surface after chemical treatment (20% water solution of NaOH).

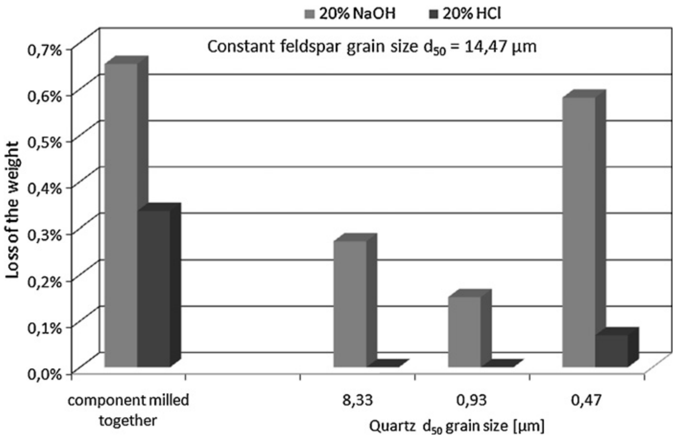

Fig. 7. The lost of weight of the glaze after 240 h corrosion in 20% water solutions HCl and NaOH in the function grain size of quartz.

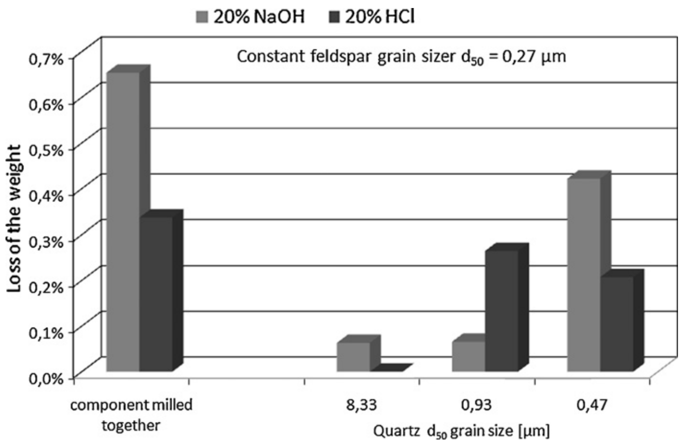

Fig. 8. The lost of weight of the glaze after 240 h corrosion in 20% water solutions HCl and NaOH in the function grain size of quartz.

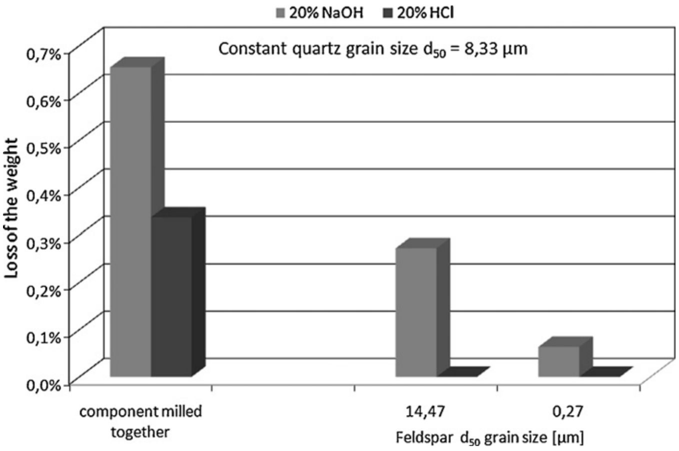

Fig. 9. The lost of weight of the glaze after 240 h corrosion in 20% water solutions HCl and NaOH in the function grain size of quartz.

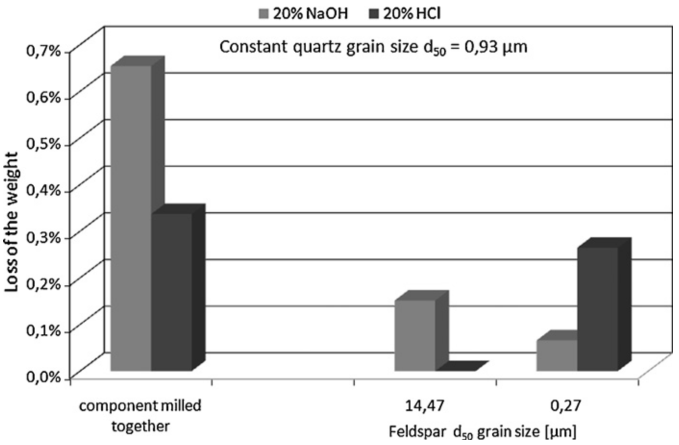

Fig. 10. The lost of weight of the glaze after 240 h corrosion in 20% water solutions HCl and NaOH in the function grain size of feldspar.

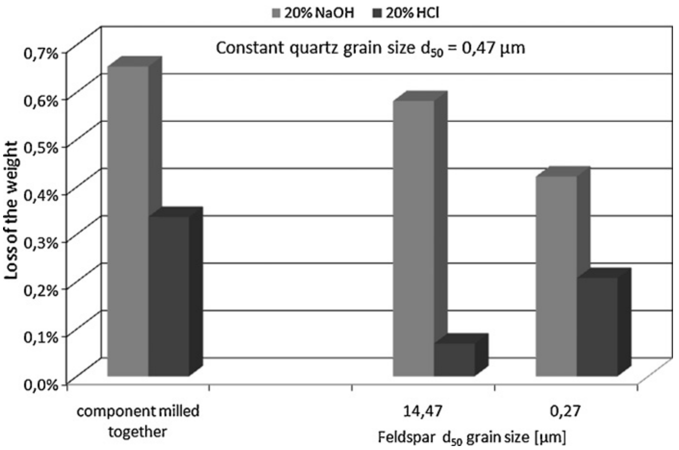

Fig. 11. The lost of weight of the glaze after 240 h corrosion in 20% water solutions HCl and NaOH in the function grain size of feldspar.

4. Conclusion

The proposed new method of selective grinding of hard raw materials with their subsequent homogenization with the remaining components seems to be an interesting alternative of producing ceramic glazes with definitely better surface properties and higher chemical resistance. However, grinding the whole raw-material glaze batch down to such a low grain size is not possible. This is so, because it would cause higher plasticity and contraction of the raw glaze applied on the body and, as a consequence, its cracking and shrinking in the firing process. In order to fully refine the new grinding technology, it will still be necessary to work out the optimal grain size ranges for hard glaze components, for specific applications and usage requirements. Whereas, implementing the described preparation method in industrial practice should not pose any problem, as commercial versions of high-energy bead-type mills are already functioning in many plants, but their capacities are not fully utilized.

The obtained results allow the two following basic conclusions to be drawn:

(1) The proper selection of the grain size of particular raw materials used for production of ceramic glazes makes it possible to obtain glazes of higher surface quality and higher chemical resistance to the action of both acid and alkaline solutions of a varying pH.
(2) The application of the gloss determination method as a means of determining the chemical resistance appears to offer a fast and economical method compared to the currently used ‘‘pencil’’ method described in the ISO 10545-13 standard.

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